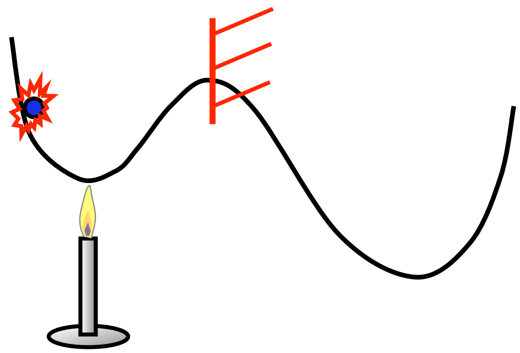
Temperature Accelerated Dynamics



A very brief introduction

Arthur F. Voter
Theoretical Division
Los Alamos National Laboratory
Los Alamos, New Mexico USA

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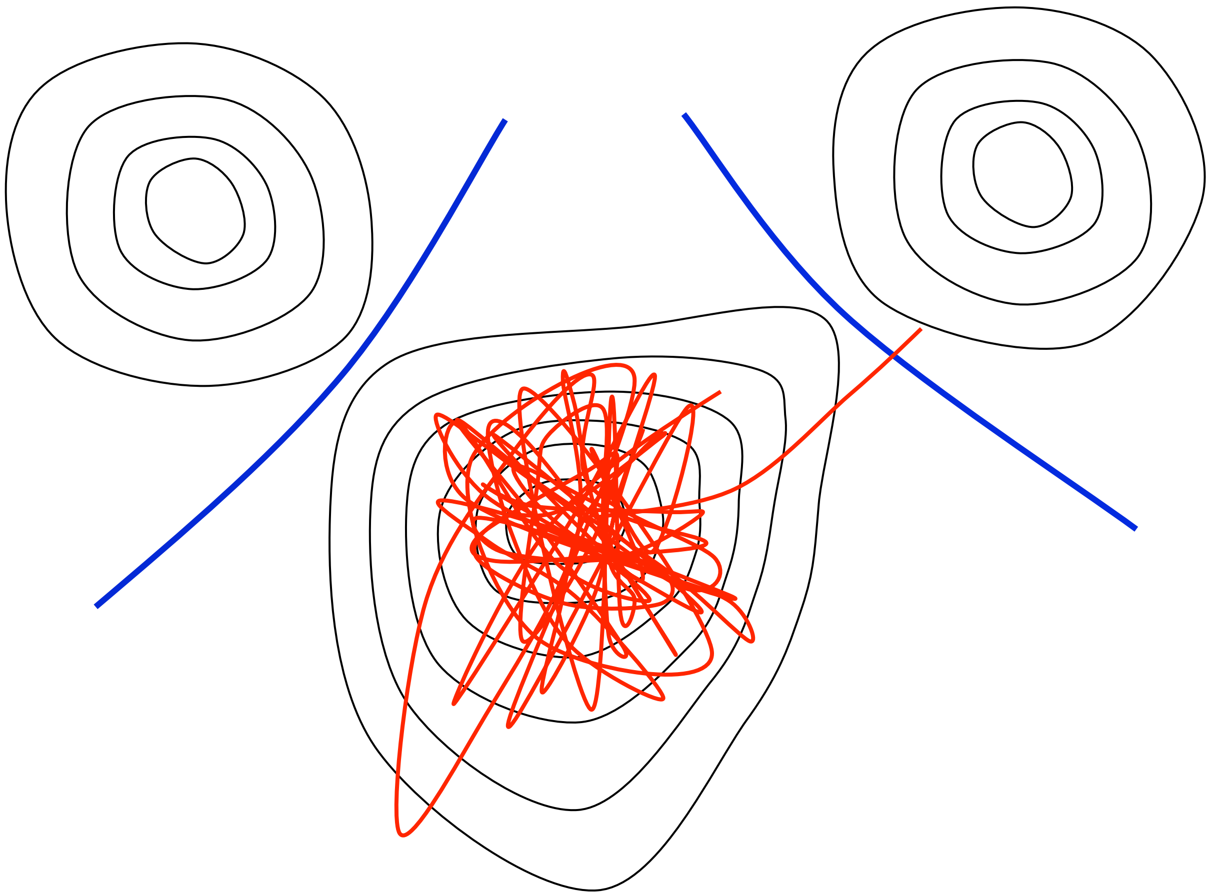
Infrequent-Event System



The system vibrates in 3-N dimensional basin many times before finding an escape path. In temperature accelerated dynamics (TAD), we raise the temperature to quickly find a few escape events. Using temperature extrapolation, we determine which event would have happened first at the low temperature.

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Temperature Accelerated Dynamics (TAD)

Concept:

Raise temperature of system to make events occur more frequently. Filter out the events that should not have occurred at the lower temperature.

Assumptions:

- infrequent-event system
- transition state theory (no correlated events)
- harmonic transition state theory (gives Arrhenius behavior)

$$k = \nu_0 \exp[-\Delta E/k_B T]$$

- all preexponentials (ν_0) are greater than ν_{min}

[Sørensen and Voter, J. Chem. Phys. 112, 9599 (2000)]

TAD Procedure

- Run MD at elevated temperature (T_{high}) in state A.
- Intercept each attempted escape from basin A
    - find saddle point (and hence barrier height)
      (e.g., using nudged elastic band method of Jonsson et al).
    - extrapolate to predict event time at T_{low}.
- Reflect system back into basin A and continue.
- When safe, accept transition with shortest time at T_{low}.
- Go to new state and repeat.

TAD temperature-extrapolated time

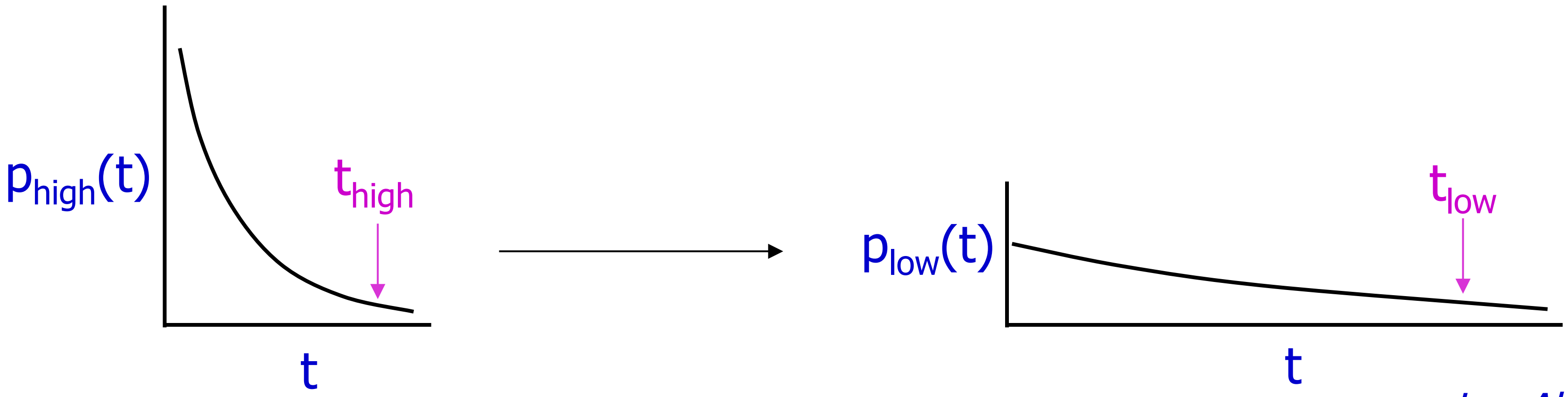
Because each rate is assumed to be Arrhenius,

$$k = \nu_0 \exp[-\Delta E/k_B T] ,$$

the time for each particular event at high T can be extrapolated to low T:

$$t_{low} = t_{high} \exp[\Delta E(1/k_B T_{low} - 1/k_B T_{high})] .$$

This time is sampled correctly from the exponential distribution at low T, mapped from the high T sample:



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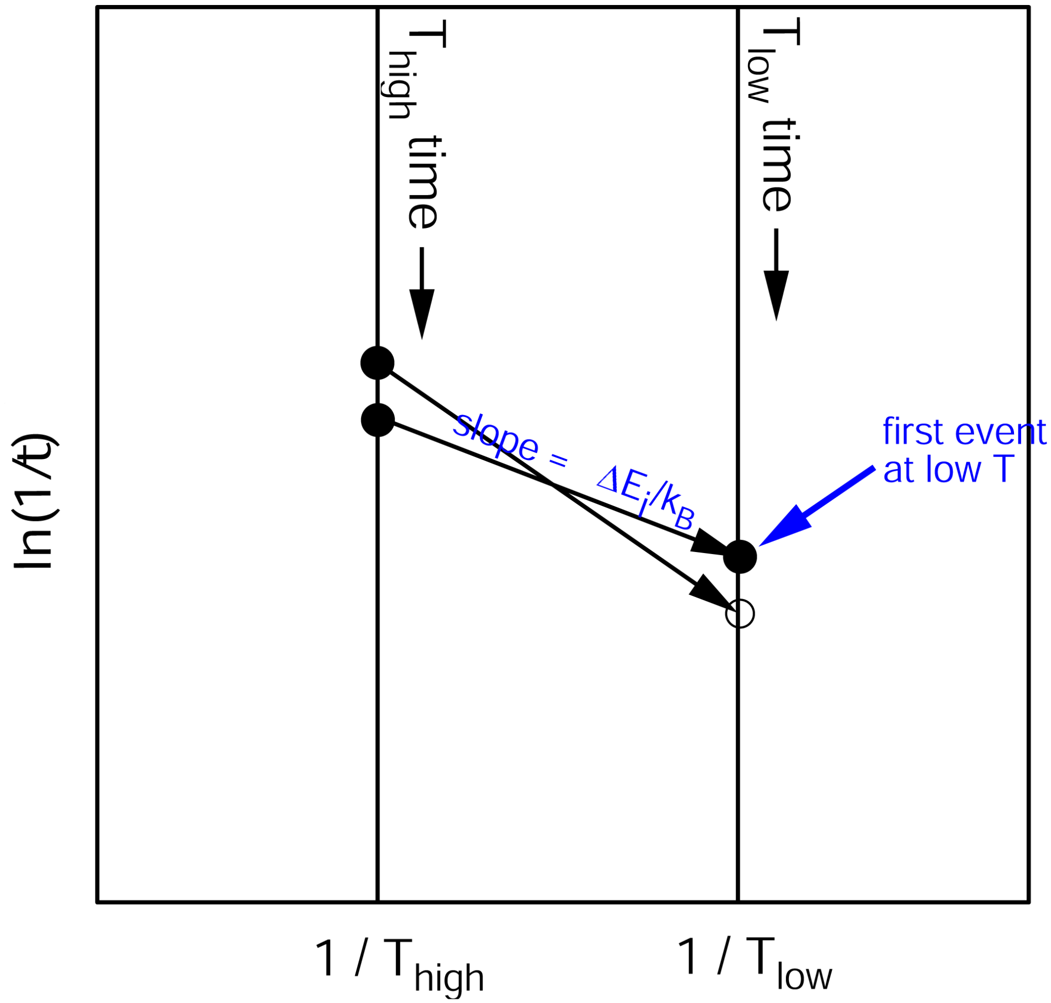
The Arrhenius view



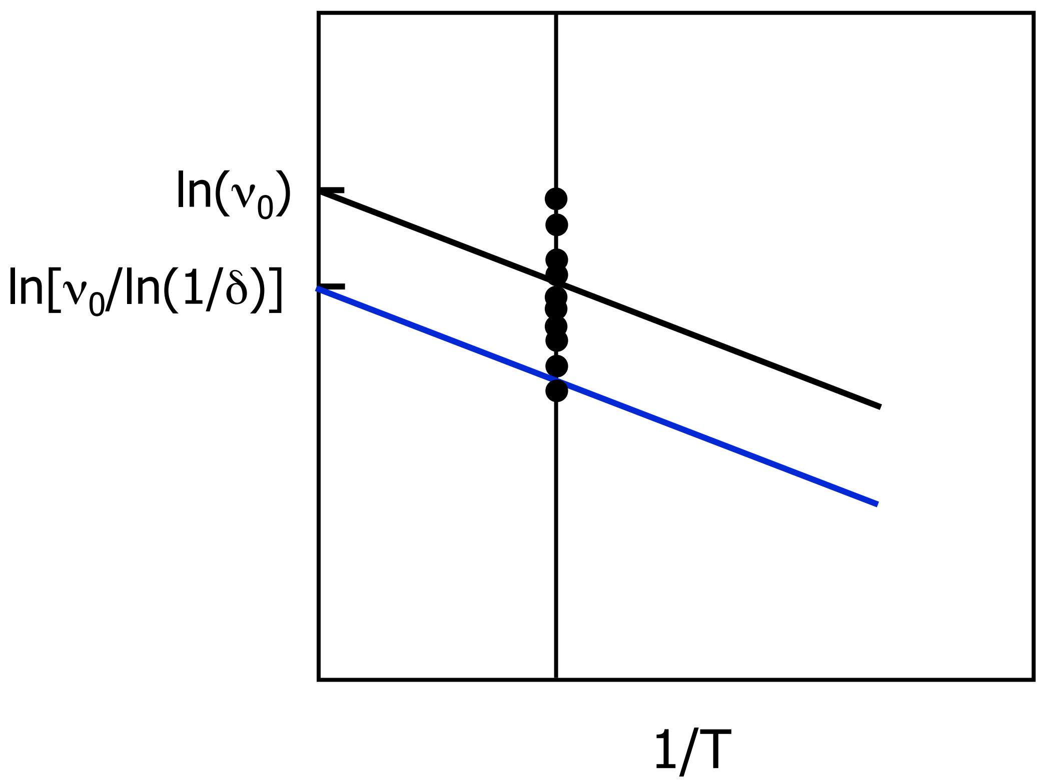
when can we stop?

The confidence line

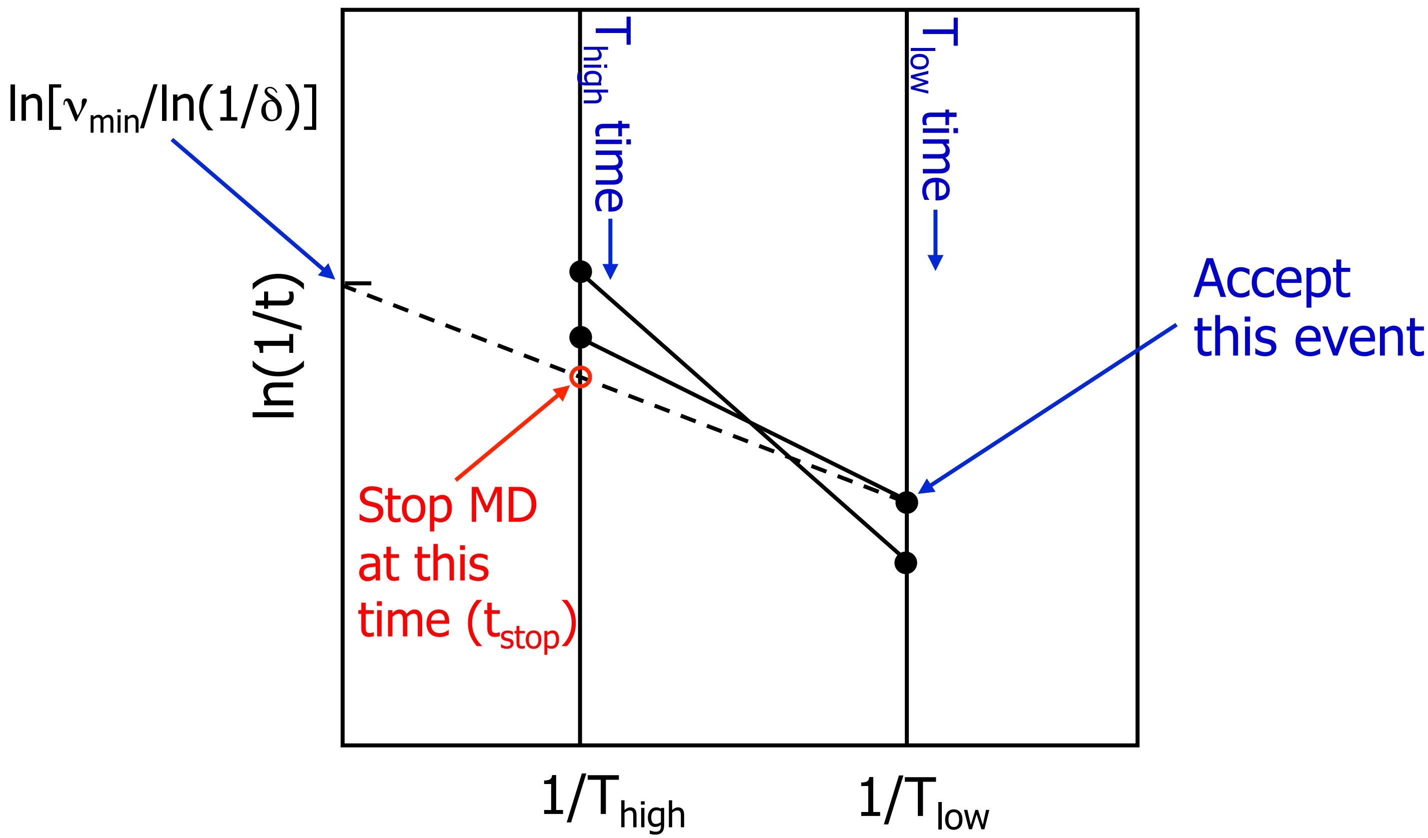
For a pathway with rate k, the time τ required to be certain with confidence $1-\delta$ that at least one escape will occur is given by

$$\tau = (1/k)\ \ln(1/\delta)$$

For an Arrhenius rate, $k = \nu_0 \exp(-E_a/k_B T)$, all but fraction δ of the first escapes will occur above the line with slope E_a and intercept $\ln[\nu_0/\ln(1/\delta)]$



TAD - when can we stop the MD and accept an event?



After time t_{stop}, with confidence 1-δ, no event can replace shortest-time event seen at low T.

Move system to this state and start again.

Exact dynamics, assuming harmonic TST, ν_{min}, uncertainty δ.

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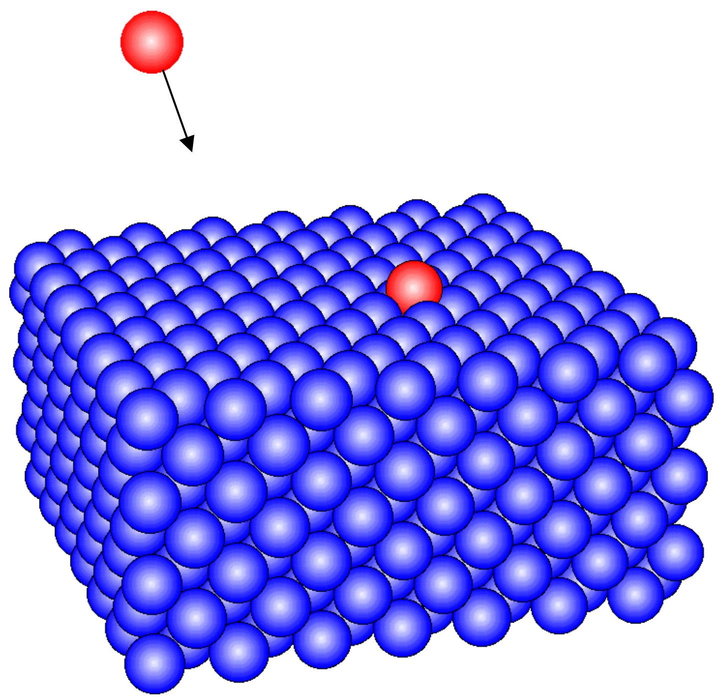
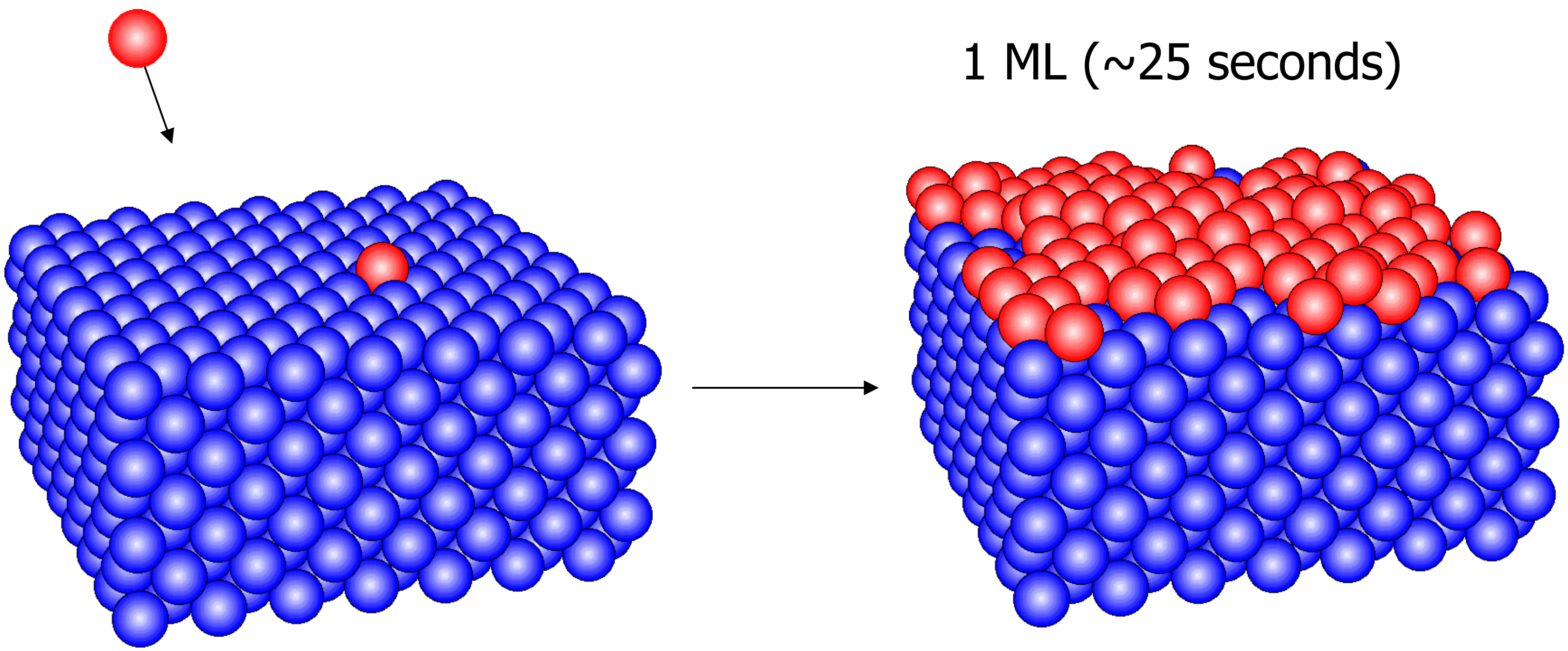
MD+TAD metal deposition simulation

- MD for each deposition event (2 ps)
- TAD for intervening time (~1 s)
- Embedded atom method (EAM) for fcc metals



MD+TAD deposition of Cu/Ag(100)

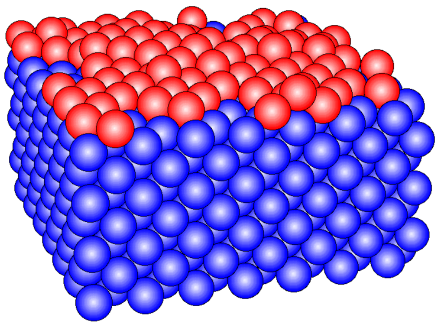
T=77K, flux= 0.04 ML/s, matching deposition conditions of Egelhoff and Jacob (1989).



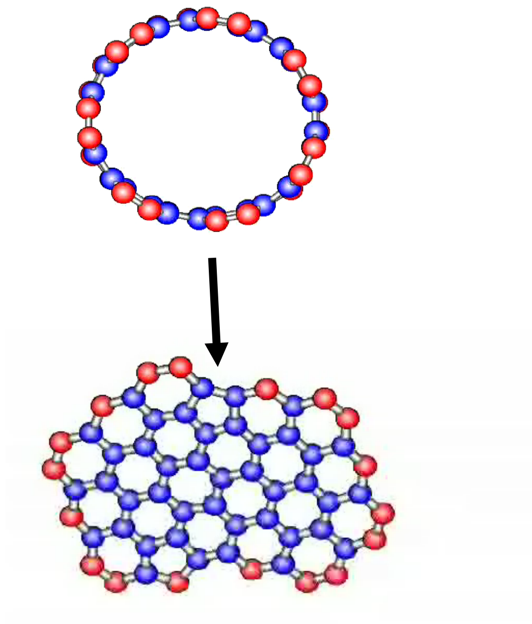
Second-layer Cu atoms exhibit novel mobility at T=77K, due to epitaxial strain of Cu on Ag(100).

Sprague, Montalenti, Uberuaga, Kress and Voter, Phys. Rev. B **66,** 20415, 2002. *Los Alamos*

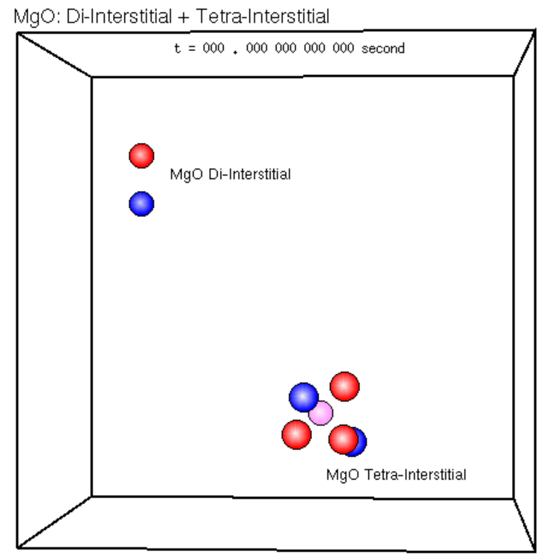
Examples of TAD Studies



Cu/Ag(100), 1 ML/25 s
T=77K, Sprague et al, 2002.

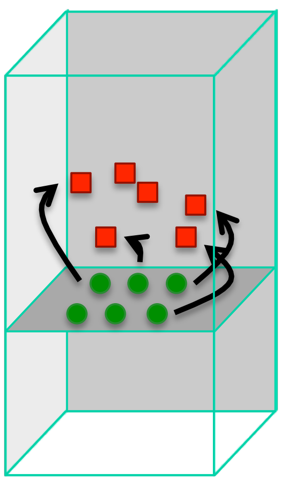


Annealing nanotube slices, μs, Uberuaga et al, 2011.

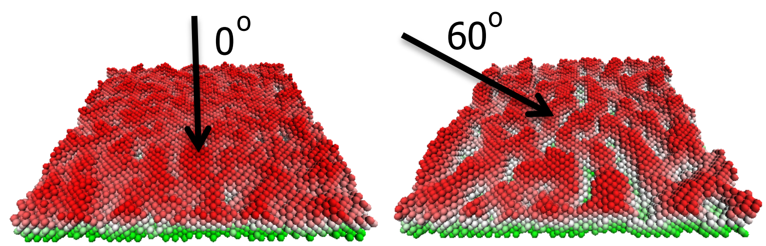


TAD simulation, Uberuaga et al, 2003

Interstitial defects in MgO, ps – s, Uberuaga et al, 2004.



Interstitial emission from GB after cascade, μs, Bai et al, Science, 2010.



Growth of Cu(001), MD+ParTAD, 5 ML/ms, Shim, Amar et al, 2008.

Recent brief review: Perez et al, Ann. Rep. Comp. Chem. **5**, 79 (2009).

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